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Europäisches Patentamt
European Patent Office
Office européen des brevets



11 Publication number:

0 376 219 B1

12

EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: 30.06.93 51 Int. Cl.⁵: H01M 8/06

21 Application number: 89123844.6

22 Date of filing: 22.12.89

54 Electric power producing system using molten carbonate type fuel cell.

30 Priority: 24.12.88 JP 324797/88

43 Date of publication of application:
04.07.90 Bulletin 90/27

45 Publication of the grant of the patent:
30.06.93 Bulletin 93/26

84 Designated Contracting States:
DE GB NL

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Description

The present invention relates to a method of producing electric power with molten carbonate type fuel cell which directly converts chemical energy of fuel to electrical energy, and to an apparatus for carrying out the method.

A method according to the first part of claim 1 and a molten carbonate type fuel cell device according to the first part of claim 9 are known from JP-A-61 24 171.

The fuel cell comprises a tile (electrolyte plate) of a porous substance filled with an electrolyte of a molten carbonate, which tile is sandwiched between a cathode electrode (oxygen plate) and an anode electrode (fuel plate), and an oxidizing gas is fed into the cathode electrode while a fuel gas is supplied into the anode electrode so as to cause a reaction between the cathode and the anode and to produce electric power.

In a case where a hydrocarbon or methanol is employed as a fuel in the electric power-producing system using the molten carbonate type fuel cell, first the fuel is reformed to a fuel gas and then fed into the anode of the fuel cell.

As the means of reforming the above-mentioned fuel, an external reformation type and an internal reformation type are popular in the art.

As the conventional external reformation type, one typical system is shown in Figure 6 of the accompanying drawings, in which a hydrocarbon (natural gas such as methane) that is used as the fuel gas to be fed into the anode b of the fuel cell a is first introduced into the reformer d, and then the hydrogen (H_2) and carbon monoxide (CO) formed therein are introduced into the anode b as the fuel gas and are partially consumed for producing electric power. On the other hand, the anode exhaust gas expelled from the anode b, as containing the non-reacted methane (CH_4), hydrogen (H_2) and carbon monoxide (CO) in addition to the carbon dioxide (CO_2) and water (H_2O) generated in the fuel cell 1, is supplied into the combustion chamber of the reformer d through a line e and is combusted therein to produce a heat necessary for reformation of the fuel gas. The CO_2 -containing gas exhausted from the combustion chamber of the reformer d passes through a line f to be combined with air A and is fed to the cathode c to be utilized for the cell reaction.

On the other hand, one typical system of the conventional internal reformation type is shown in Figure 7, in which the reformer d is built in the fuel cell a so that the heat from the fuel cell a is directly utilized for the reforming reaction in the reformer d, the anode exhaust gas to be discharged from the anode b is composed of the same components as those constituting the anode exhaust gas in the

case of the above-mentioned external reformation type system and contains the non-reacted CH_4 , H_2 and CO. The hydrogen (H_2) is separated from the anode exhaust gas in a hydrogen-separator g and is recirculated to the reformer d through a line h via a fuel feed line i to the reformer d while the remaining CH_4 , CO and the non-separated H_2 are combusted in a catalyst combusting device j and are fed into the cathode c together with the air A through a line k.

However, in both these external reformation type and internal reformation type systems, the non-reformed CH_4 contained in the gas exhausted from the anode b and CO and H_2 not reacted in the fuel cell are combusted and then fed into the cathode c together with the air. Therefore, these systems have a drawback that the CH_4 , CO and H_2 can not be completely utilized in the cell reaction but are combusted to be converted into a heat energy. Hence, the power-producing efficiency is poor. In addition, the methane (CH_4) which is not reformed in the reformer d would cause a deterioration of the power-producing efficiency. Such a deterioration has to be counterbalanced by a certain measure. For this purpose, generally an amount of the steam for reformation is increased and the reaction temperature for reformation is elevated. Still another problem is that the H_2 and CO not used in the fuel cell would also cause a depression of the power-producing efficiency. If the utilization factor of those gases is raised, the cell potential would drop, and therefore, a part of these H_2 and CO are inevitable to remain as they are not used. Moreover, there is still another problem that the non-combusted gas from the fuel cell contains carbon dioxide gas which is a low caloric gas. Therefore, an expensive catalyst combustion device is necessary for combusting the gases.

One object of the present invention is to improve the power-producing efficiency of a fuel cell, in which the anode exhaust gas as exhausted from the anode electrode of the cell is introduced into the reformer, after carbon dioxide gas has been removed from the exhaust gas, and then recirculated into the anode of the fuel cell.

Another object of the present invention is to provide a system of a fuel cell, in which the carbon dioxide gas as removed from the anode exhaust gas is fed, following a treatment step in a combustion device, to the cathode electrode together with air.

These objects are attained by a method and an apparatus as set forth in claims 1 and 9, respectively.

In this system, the carbon dioxide gas separator may have a carbon dioxide gas absorber, which includes a solution containing alkali, salt or amine as a carbon dioxide gas absorptive liquid, and an

absorbed liquid regenerator.

In the system, the fuel gas as reformed in the reformer is fed into the anode of the molten carbonate type fuel cell and is used for electrochemical reaction. The anode exhaust gas exhausted from the anode electrode is introduced into the carbon dioxide separator in which the carbon dioxide is separated from the exhaust gas. The thus separated carbon dioxide gas is fed into the cathode of the fuel cell together with air, whereas the anode exhaust gas from which carbon dioxide gas has been removed is recirculated to the fuel cell via the reformer. The reformer may be either such that almost all the anode exhaust gas is introduced thereinto so as to heat the reforming part or such that the cathode exhaust gas of the fuel cell is introduced thereinto to give the heat necessary for reformation. That is, the reformer may be either such a type having no combustion chamber or a type having a combustion chamber. Furthermore, the reformer may be a type integrally provided to the fuel cell, i. e., the reformer used in the internal reformation type fuel cell. According to the present invention means are provided for combusting a part of the anode exhaust gas from the anode dioxide separator together with an air mixture of the separated CO₂ and thereafter introducing the gas into the cathode of the fuel cell.

The anode exhaust gas discharged from the anode electrode contains carbon dioxide gas and water generated in the fuel cell, in addition to the non-used fuel, hydrogen and carbon monoxide. However, since almost all the carbon dioxide gas is separated from the exhaust gas and is fed into the cathode together with air and since the anode exhaust gas from which carbon dioxide gas has been removed is recirculated to the anode via the reformer, the fuel which is not used in the fuel cell can be completely and effectively consumed and therefore the power-generating efficiency is improved.

Figure 1

is a systematic diagram showing one embodiment of the electric power-producing molten carbonate type fuel cell system of the present invention;

Figure 2

is a schematic view of the reformer as used in Figure 1;

Figures 3, 4 and 5

are outline views to show other types of the reformer applicable to the present invention respectively;

Figure 6

is a schematic diagram showing a conventional external reformation type electric power-producing fuel cell system; and

Figure 7

is a schematic diagram showing a conventional internal reformation type electric power-producing fuel cell system.

Now, preferred embodiments of the present invention will be explained with reference to the attached drawings.

In Figure 1, numeral 1 designates a molten carbonate type fuel cell in which a molten carbonate-impregnated tile 2 is sandwiched by an anode electrode 3a and a cathode electrode 4a. Both plates 3a and 4a have an anode chamber 3 and a cathode chamber 4 respectively. Numeral 5 designates a reformer in which the anode exhaust gas releases a heat necessary for reformation and the fuel gas is thereby reformed to an anode gas. The reformer 5 is, as shown in Figure 2, filled with reforming catalyst 5a, and the above-mentioned exhaust gas releases a heat sufficient to maintain the reforming reaction. Numeral 6 denotes a heater provided in the course of a feed line 7 for fuel gas and steam. Numeral 8 is a line for feeding the anode gas reformed in the reformer 5 to the anode chamber 3. Numeral 9 designates an anode exhaust gas line extending from the anode chamber 3. Numeral 10 is an anode exhaust gas branch line which is branched from the anode gas line 9 so as to introduce the anode exhaust gas to the inlet of reformer 5 thereby to impart the necessary heat hereto. Numeral 11 is a cooler provided downstream of the connected point of the branch line 10 with the anode exhaust gas line 9. Numeral 12 is a condenser provided in the anode exhaust gas line 9 downstream of the cooler 11. Numeral 13 is a carbon dioxide gas separator. The carbon dioxide gas separator 13 is, as one example, composed of an absorption column 13a for absorbing carbon dioxide by a carbon dioxide gas absorber, a regeneration column 13b for regenerating the aqueous diethanolamine, an aqueous amine solution feed line 13c for feeding the aqueous diethanolamine solution to the regeneration column 13b, and an aqueous amine solution recirculation line 13d for recirculating to the absorption column 13a the aqueous diethanolamine solution as regenerated in the regeneration column 13b. The carbon dioxide gas absorber may be an aqueous diethanolamine solution, aqueous alkali salt solution such as potassium carbonate or a mixture of such solutions.

Numeral 14 is a circulation gas line for recirculating the remaining gases such as methane and hydrogen, which are taken out from the absorption column 13a after carbon dioxide gas has been removed in the carbon dioxide separator 13, to the upstream of the heater 6 as provided in the fuel and steam feed line 7. Numeral 15 is a gas heater as provided in the course of the circulation gas line 14. Numeral 16 is an air feed duct as connected to the bottom of the regeneration column 13b of the

carbon dioxide gas separator 13. Numeral 17 is an air feed line for taking out from the regeneration column 13b the carbon dioxide gas-containing air as separated in carbon dioxide gas separator 13 and feeding the same to the cathode chamber 4 of the fuel cell 1. Numeral 18 is an air heater as provided in the course of the carbon dioxide gas feed line 17. Numeral 19 is a water-treating boiler. Numeral 20 is a line for conveying the water from the condenser 12 to the water-treating boiler 19. Numeral 21 is a steam feed line for conveying the steam as separated in the water-treating boiler 19 and over-heated in a heater to an over-heated steam to an upper stream part of the fuel feed line 7. Numeral 23 is an exhaust line for discharging any excessive water out of the system. Numeral 24 is a cathode exhaust gas line for the gas exhausted from the cathode chamber 4 of the fuel cell 1.

In one example to discribed hereunder, methane is employed as the hydrocarbon or alcohol-containing fuel gas to be fed into the fuel feed line 7. Methane is pre-heated in the heater 6 and then reformed in the reformer 5 to give hydrogen gas. Carbon monoxide gas and methane in the reformer 5 is obtained from the gas as exhausted from the anode chamber 3 in this example. The anode gas reformed in the reformer 5 is introduced into the anode chamber 3 of the fuel cell 1 via the feed line 8 and is utilized for electro-chemical reaction therein. The gas to be exhausted from the anode chamber 3 contains carbon dioxide gas (CO_2) and water (H_2O) which are generated in the fuel cell, in addition to the non-used methane (CH_4), hydrogen (H_2) and carbon monoxide (CO). Most of these gases are transported to the reformer 5 via the anode exhaust gas branch line 10 branched from the anode exhaust gas line 9 while a part of the same is led to the cooler 11 and the condenser 12 via the anode exhaust gas line 9 whereupon the gas fraction is introduced into the absorber 13a of the carbon dioxide gas separator 13. Most of the carbon dioxide gas among the gas fraction transmitted into the absorber 13a is absorbed in the aqueous diethanolamine solution as being brought into contact therewith in the absorber 13a and is thereby removed, while the gases remaining after separation of the carbon dioxide gas which contain methane, a trace amount of carbone dioxide and hydrogen are taken out from the top of the absorber 13a through the residual gas line 14, preheated in the circulation gas heater 15, transported to the upper stream of the heater 6, reformed to an anode gas in the reformer 5 and thereafter transported to the anode chamber 3 of the fuel cell 1 in which the gas undergoes the cell reaction. Accordingly, the electric power producing efficiency is raised. The aqueous amine solution which has absorbed the carbon dioxide gas in the absorption column 13a is

fed to the regeneration column 13b via the aqueous amine solution feed line 13c, in which the carbon dioxide gas is stripped with the air supplied from the air feed duct 16 and the aqueous amine solution from which the carbone dioxide gas has been removed is recirculated to the absorption column 13a via the aqueous amine solution recirculation line 13d and is used therein for absorbing carbon dioxide gas. The air which has contained carbon dioxide gas in the regeneration column 13b is preheated in the air preheater 18 and then supplied into the cathode chamber 4 of the fuel cell 1, in which the oxygen gas and carbon dioxide gas are utilized for electrochemical reaction.

The water separated in the condenser 12 is transported to the water-treating boiler 19 via the line 20 whereas the steam is heated to a steam by the heater 22 in the steam feed line 21 and introduced into the fuel feed line 7 to be utilized in the reformer 5 as a reforming steam. The excessive water in the water treating boiler 19 is expelled out of the system via the discharge line 23.

In accordance with the present invention, as mentioned above, since the non-used methane and hydrogen contained in the anode exhaust gas taken out through the anod exhaust gas line 9 are recovered by the carbon dioxide gas separator 13 and is recirculated into the fuel cell 1 via the reformer 5 to be utilized for the electrochemical reaction therein, the power producing efficiency may be noticeably improved as compared with the conventional system in which the non-used gases are effectively not utilized in the cell reaction but are merely combusted. In this case, it is satisfactory that the methane-reforming efficiency in the reformer 5 be low since the methane can be recycled. Accordingly, the heat from the cell may be easily utilized as the heat necessary for the reformation reaction.

A part of the residual gases taken out from the absorption column 13a, which include methane and hydrogen, is branched from the residual gas branch line 26, and introduced into and burned in the combustion device 27 provided in the course of the air feed line 17. The resulting combustion gas is transported into the cathode chamber 4. This embodiment has various advantages that the temperature of the cathode gas is elevated and the power-producing efficiency is thereby improved, and accumulation of trace components which would be caused by circulation of the anode gas for a long period of time is prevented.

The system illustrated in Figure 4 is such that the exhaust gas from the anode chamber 3 is circulated to the reformer 5 via the anode exhaust gas branch line 10 extending from the anode exhaust gas line 9. in which the heat from the anode exhaust gas is utilized for the reformation reaction.

According to the experiments by the present inventor where the flow amount of the gas to be circulated to the reformer 5 via the anode exhaust gas branch line 10 was made three times as much as that of the gas to be transported to the carbon dioxide gas separator 13 through the anode exhaust gas line 9, and the anode outlet temperature was 700 degrees C ($^{\circ}\text{C}$) and the temperature in the fuel feed line 7 was 550 $^{\circ}\text{C}$, the outlet temperature of the reformer 5 was 607 $^{\circ}\text{C}$ and the reformed percentage of methane was 25.7%. Accordingly, even though the reformed percentage of methane is small, the power-producing efficiency is high in the method of the present invention since all the non-reformed methane is recirculated to the reformer and is utilized for the cell reaction.

Only the carbon dioxide gas is removed from the gases introduced into the carbon dioxide gas separator 13 through the anode exhaust gas line 9. Here, when an aqueous 30 wt.% diethanolamine solution is employed as a solution for absorbing the carbon dioxide gas, 85.8 % of the carbon dioxide gas in the anode exhaust gas may be absorbed or removed in the absorption column 13a. The remaining gases thus separated include methane, hydrogen, carbon monoxide, carbon dioxide and water and those gases are entirely recirculated to the reformer 5. Therefore, there is no fuel loss. When an air which corresponds to the oxygen utilization percentage of 50 % is utilized as the stripping gas in the regenerator column 13b, all the carbon dioxide gas absorbed in the absorption column 13a can be stripped and transported to the cathode 4 together with air. Accordingly, any additional heat, for example by steam, is unnecessary for regeneration.

Figure 3 through Figure 5 show still other embodiments of the reformer of the present invention.

Figure 3 shows a modified reformer 28, and the cathode exhaust gas from the line 24 is introduced into the heating part 28b of the reformer 28 in order that the heat necessary for reformation in the reforming part 28a may be obtained from the gas as taken out from the cathode chamber 4, whereas the gas which has given the heat to the reformation reaction is then transported to the cathode chamber.

Figure 4 shows another reformer 29. In this case, the heat necessary for reformation in the reforming part 29a of the reformer 29 is obtained from a combustion in the combustion part 29b, and for this, a part of the anode exhaust gas is introduced into the combustion part 29b as a combustion gas while a part of the air to be supplied to the cathode is introduced into the combustion part 29b via the line 29c, whereupon the gas which has given the heat for the reformation reaction is then fed into the cathode.

Figure 5 shows the internal reformation type fuel cell 30, in which the electrolyte tile 2 is sandwiched between the anode electrode 3a and the cathode electrode 4a, a plurality of anode/tile/cathode units are stacked via separator plates 31 with the reformer 32 being inserted in an arbitrary separator plate 31. Each separator plate 31 defines the anode chamber 3 on one face thereof and the cathode chamber 4 on the other face thereof. The anode gas reformed in the reformer 32 is supplied into the anode chambers 3 through the line 8 formed inside the fuel cell, and the anode exhaust gas from the respective chambers 3 are collected and discharged through the exhaust gas line 9. The cathode gas coming from the line 17 is distributed into the respective cathode chambers 4 and then flows into the line 24.

In the internal reformation type fuel cell 30, the reformation reaction temperature is maintained by the heat derived from the anode gas in the anode chamber 3 contacting the reformer and the heat derived from the cathode gas in the cathode chamber 4 which also contacts the reformer. The internal reformation type fuel cell 30 of Figure 5. may be employed in a power-generation apparatus, which is the same as that of Figure 1, except that the reformer is located in the fuel cell.

In the case of the conventional internal reformation type reformer as shown in Figure 7, it is necessary that the reforming part is directly provided inside the anode chamber, since the efficiency for reformation of methane has to be raised. This means that the conventional type reformer has a drawback that the reforming catalyst is likely deteriorated by the electrolyte. On the contrary, since the efficiency for reformation of methane is not an important factor in the system of the present invention, the reforming part 30a and the anode chamber 30b can be provided separately and heat exchange may be effected indirectly therebetween. Therefore, the longevity of the reforming catalyst is prolonged.

The reformer shown in Figure 3 or Figure 4 may be employed in place of the reformer 5 of Figure 1. In addition, various aqueous solutions of other amines or alkali metal salts or mixtures thereof may be employed as the carbon dioxide gas-absorbing solution, in place of the aqueous diethanolamine (DEA) solution.

As mentioned above, the anode exhaust gas exhausted from the anode of the fuel cell is transported to the carbon dioxide gas separator and the carbon dioxide is separated from the exhaust gas. The residual gas not containing carbon dioxide gas is then fed into the anode of the fuel cell via the reformer, whereas the carbon dioxide gas is supplied into the cathode of the fuel cell together with air. Accordingly, the fuel not used in the fuel cell

may be efficiently recirculated and completely utilized for the cell reaction so that the power-producing efficiency is improved. In addition, when methane is used as a fuel, the carbon dioxide gas in the anode outlet gas may be separated and all the methane may be recirculated to the reformer. This means that the fuel utilization efficiency does not drop even though the methane reformation is low. Accordingly, a design of the reformer can be simplified. Moreover, the cathode inlet temperature may be raised due to combustion by a burner so as to further improve the fuel cell characteristics. In this case, the anode exhaust gas containing less amount of carbon dioxide is obtained so that an expensive catalyst combustion device is unnecessary.

Claims

1. A method of producing electric power with a molten carbonate type fuel cell (1) wherein an anode gas is fed into an anode chamber (3) of the fuel cell (1) and a cathode gas is fed into a cathode chamber (4) thereof, wherein the method comprises the steps of:
 - (A) introducing a fuel gas and steam into a reformer (5) so as to reform the fuel gas with the steam to give an anode gas containing H_2 and CO and then feeding the resulting anode gas into the anode chamber (3) of the fuel cell (1);
 - (B) separating carbon dioxide gas from the anode exhaust gas as exhausted from the anode chamber; and
 - (C) recirculating the anode exhaust gas from which carbon oxide gas has been removed in the step (B), to the anode chamber (3) via the reformer as the anode gas; **characterized by**
 - (D) introducing into air the carbon dioxide gas as separated from the anode exhaust gas and feeding the resulting mixed gas into a combustion device (27) while part of the anode exhaust gas, from which carbon dioxide gas has been removed, is fed into said combustion device (27) and is combusted there, and the outlet gas from the combustion device (27) is fed into the cathode chamber (4) as cathode gas.
2. The method of claim 1, **characterized** in that the step (B) is effected by a vapour-liquid contact between the anode exhaust gas and a carbon dioxide-absorbing liquid.
3. The method of claim 2, **characterized** in that the anode exhaust gas is cooled prior to the vapour-liquid contact with the carbon dioxide gas-absorbing liquid, the steam in the anode exhaust gas is condensed and separated, and thereafter the vapour-liquid contact between the anode exhaust gas and the carbon dioxide gas-absorbing liquid is effected.
4. The method of claims 2 or 3, **characterized** in that the carbon dioxide-absorbing liquid is an aqueous solution of an amine such as diethanolamine, aqueous alkali salt solution such as potassium carbonate or a mixture of the aqueous alkali salt solution and the aqueous amine solution.
5. The method one of claims 2 to 4, **characterized** in that the carbon dioxide gas-absorbing liquid which has absorbed carbon dioxide gas is isolated from a flow line of the anode exhaust gas while air is blown into the carbon dioxide gas-absorbing liquid which has absorbed carbon dioxide gas to release carbon dioxide gas from the liquid and the thus released gas which may be a mixture of carbon dioxide gas and air is fed into the cathode chamber (4) as cathode gas.
6. The method of one of claims 1 to 5, **characterized** in that the anode exhaust gas or cathode gas is utilized as the heat source for maintaining the reforming temperature in a reformer (5).
7. The method of one of the claims 3 to 6, **characterized** in that a part of the condensed water as separated is heated to a steam and is mixed with the fuel gas.
8. The method of claim, **characterized** in that the fuel gas, such a methane, is reformed with steam in a reformer (5) so as to obtain the anode gas and the anode gas is supplied into the anode of the fuel cell, and the anode exhaust gas from which carbon dioxide has been separated in the step (B) is fed into the reformer (5) together with the fuel gas and steam and then recirculated to the anode chamber (3).
9. An apparatus for producing electric power comprising:
 - at least one molten carbonate fuel cell (1) including a molten carbonate-impregnated electrolyte tile (2) as sandwiched between an anode electrode (3a) and a cathode electrode (4a) both of which electrodes (3a, 4a) being provided with an anode chamber (3) and a cathode chamber (4) for feeding an anode gas and a cathode gas thereto, respectively;

- an anode gas feed line (8) and an anode exhaust gas line (9) as connected with an inlet and an outlet of the anode chamber (3) of the fuel cell (1) for introducing and exhausting the anode gas thereinto and therefrom, respectively;
- a cathode gas feed line (17) and a cathode exhaust line (24) as connected with an inlet and an outlet of the cathode chamber (4) of the fuel cell (1) for introducing and exhausting the cathode gas thereinto and therefrom, respectively;
- means (7) for feeding a fuel gas and a steam into the anode gas feed line (8); and
- a carbon dioxide gas separator (13) **characterized** in that the carbon dioxide gas separator (13) includes an absorption column (13a) in which the anode exhaust gas from the anode exhaust gas line (9) is brought into contact with a carbon dioxide-absorbing liquid by vapour-liquid contact and the thus contacted gas is recirculated to said reformer (5), and a regeneration column (13b) connected with the cathode gas feed line (17) in which the carbon dioxide-absorbed liquid from said absorption column (13a) is introduced and the liquid is tripped with air (16) as being fed from the cathode gas feed line (17) so as to release carbon dioxide gas from the liquid while the liquid from which the carbon dioxide gas has been stripped and released is recirculated to said absorption column (13a); and
- that the apparatus further comprises a combustion device (27) connected with the cathode gas feed line (17) between the regeneration column (13b) of the carbon dioxide gas separator (13) and the cathode chamber (4) in which combustion device (27) a part of the anode exhaust gas coming from said absorption column (13a) to the reformer (5) is introduced and is combusted with the air (16) taken from the cathode gas feed line (17), so as to produce a cathode gas.
10. The apparatus as claimed in claim 9, **characterized** in that the anode exhaust gas line (9), extending from the anode chamber (3) to the absorption column (13a) is connected with condensing and separating means (12) for isolating the steam from the anode exhaust gas.
11. The apparatus as claimed in claim 9 or 10, **characterized** in that the anode exhaust gas or cathode exhaust gas is introduced into the reformer (5) as the heat source for maintaining the reforming temperature.

12. The apparatus as claimed in claim 10 or claims 10 and 11, **characterized** in that the condensing and separating means (12) is connected with a steam feed line (21) through which the steam converted from a part of the condensed and separated water by a heater (22) is recirculated to an upper stream part of the anode gas feed line (8).
13. The apparatus as claimed in claim 10 or 12, **characterized** in that the condensing and separating means (12) is connected with a steam feed line (21) through which the steam, as converted from a part of the condensed and separated water by a heater (22), is recirculated to the fuel gas and steam feed line (7).
14. The apparatus as claimed in any one of claims 9 to 13, **characterized** in that it comprises a stack of internal reformation type fuel cells (30), and that the reformer (32) is provided between an arbitrary pair of anode chamber (3) and cathode chamber (4) for feeding a reformed gas into the anode chamber (3).

Patentansprüche

1. Verfahren zur Erzeugung elektrischer Energie mit einer Brennstoffzelle (1) des Karbonatschmelzentyps, wobei ein Anodengas in eine Anodenkammer (3) und ein Kathodengas in eine Kathodenkammer (4) derselben eingeleitet wird, umfassend folgende Schritte:
- A) Einleiten von Brennstoffgas und Dampf in einen Reformer (5), um das Brennstoffgas mit dem Dampf zu reformieren und ein H₂ und CO enthaltendes Anodengas zu erzeugen, und anschließendes Einleiten des resultierenden Anodengases in die Anodenkammer (3) der Brennstoffzelle (1);
- B) Trennen von Kohlendioxidgas von dem Anodenabgas, das aus der Anodenkammer abgeführt wird; und
- C) Rückführen des Anodenabgases, von dem Kohlendioxid in Schritt B) abgetrennt wurde, als Anodengas über den Reformer zu der Anodenkammer (3);
- gekennzeichnet durch**
- D) Einleiten des von dem Anodenabgas abgetrennten Kohlendioxidgases in Luft und Zuführen des resultierenden Mischgases in eine Verbrennungseinrichtung (27), während ein Teil des Anodenabgases, von dem Kohlendioxid abgetrennt worden ist, der Verbrennungseinrichtung (27) zugeführt und verbrannt wird, wobei das Abgas der Verbrennungseinrichtung (27) der Kathodenkammer (4) als Kathodengas zugeführt wird.



2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß Schritt B) durch einen Dampf-Flüssigkeit-Kontakt zwischen dem Anodenabgas und einer Kohlendioxidgas absorbierenden Flüssigkeit ausgeführt wird. 5

3. Verfahren nach Anspruch 2, **dadurch gekennzeichnet**, daß das Anodenabgas vor dem Dampf-Flüssigkeit-Kontakt mit der Kohlendioxidgas absorbierenden Flüssigkeit gekühlt wird, wobei der Dampf in dem Anodenabgas kondensiert und abgetrennt wird, und daß anschließend der Dampf-Flüssigkeit-Kontakt zwischen dem Anodenabgas und der Kohlendioxidgas absorbierenden Flüssigkeit hergestellt wird. 10 15

4. Verfahren nach Anspruch 2 oder 3, **dadurch gekennzeichnet**, daß die Kohlendioxid absorbierende Flüssigkeit eine wässrige Lösung eines Amines wie beispielsweise Diäthanolamin, eine wässrige Lösung eines Alkalisalzes wie Kaliumkarbonat oder eine Mischung der wässrigen Alkalisalzlösung oder der wässrigen Aminlösung ist. 20 25

5. Verfahren nach einem der Ansprüche 2 bis 4, **dadurch gekennzeichnet**, daß die Kohlendioxidgas absorbierende Flüssigkeit, welche Kohlendioxid absorbiert hat, von einer Strömungsleitung des Anodenabgases isoliert wird, während in die Kohlendioxidgas absorbierende Flüssigkeit, welche Kohlendioxid absorbiert hat, Luft eingeblasen wird, um das Kohlendioxid von der Flüssigkeit zu trennen, und daß das so freigegebene Gas, das eine Mischung von Kohlendioxid und Luft sein kann, der Kathodenkammer (4) als Kathodengas zugeführt wird. 30 35 40

6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet**, daß das Anodenabgas oder Kathodengas als Wärmequelle zur Aufrechterhaltung der Reformierungstemperatur in einem Reformer (5) verwendet wird. 45

7. Verfahren nach einem der Ansprüche 3 bis 6, **dadurch gekennzeichnet**, daß ein Teil des abgetrennten kondensierten Wassers bis zum Verdampfen erwärmt und mit dem Brennstoffgas gemischt wird. 50

8. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß das Brennstoffgas wie beispielsweise Methan in einem Reformer (5) mit Dampf reformiert wird, um so das Anodengas zu erhalten, das der Anode der Brennstoffzelle zugeführt wird, und daß das Anodenabgas, aus dem Kohlendioxid in Schritt B) abgetrennt wurde, in den Reformer (5) zusammen mit dem Brennstoffgas und Dampf eingeleitet und anschließend zu der Anodenkammer (3) zurückgeführt wird. 55

9. Vorrichtung zum Erzeugen elektrischer Energie, umfassend: mindestens eine Karbonatschmelzen-Brennstoffzelle (1) umfassend eine mit einer Karbonatschmelze getränkte Elektrolytplatte (2), die zwischen einer Anode (3a) und einer Kathode (4a) eingeschlossen ist, wobei beide Elektroden (3a, 4a) eine Anodenkammer (3) bzw. eine Kathodenkammer (4) zur Aufnahme eines Anodengases bzw. eines Kathodengases haben; eine Anodengaszuführleitung (8) und eine Anodenabgasleitung (9), die mit einem Einlaß bzw. einem Auslaß der Anodenkammer (3) der Brennstoffzelle (1) zum Einführen bzw. Abführen des Anodengases in die Anodenkammer bzw. aus dieser verbunden sind; eine Kathodengaszuführleitung (17) und eine Kathodenabgasleitung (24) die mit einem Einlaß bzw. einem Auslaß der Kathodenkammer (4) der Brennstoffzelle (1) zum Einführen bzw. Abführen des Kathodengases in die Kathodenkammer bzw. aus dieser verbunden sind; Mittel (7) zum Zuführen von Brennstoffgas und Dampf in die Anodengaszuführleitung (8); und einen Kohlendioxidgasseparator (13), **dadurch gekennzeichnet**, daß der Kohlendioxidgasseparator (13) eine Absorptionssäule (13a) umfaßt, in der das Anodenabgas aus der Anodenabgasleitung (9) über einen Dampf-Flüssigkeit-Kontakt in Kontakt mit einer Kohlendioxid absorbierenden Flüssigkeit gebracht wird und das so kontaktierte Gas zu dem Reformer (5) zurückgeführt wird, daß der Kohlendioxidgasseparator (13) ferner eine mit der Kathodengaszuführleitung (17) verbundene Regenerierungssäule (13b) umfaßt, in welche die Kohlendioxid absorbierende Flüssigkeit der Absorptionssäule (13a) eingeführt und in der die Flüssigkeit mit Luft (16) vermischt wird, die über die Kathodengaszuführleitung (17) zugeführt wird, um so das Kohlendioxidgas von der Flüssigkeit abzutrennen, während die von dem Kohlendioxidgas befreite Flüssigkeit zur Absorptionssäule (13a) zurückgeleitet wird; und daß die Vorrichtung ferner eine Verbrennungseinrichtung (27) umfaßt, die mit der Kathodengaszuführleitung (17) zwischen der Regenerierungssäule (13b) des Kohlendioxidgasseparators (13) und der Kathodenkammer (4) verbunden ist und in die ein Teil des von der Absorptionssäule (13a) zu dem Reformer (5) geleiteten Anodenabgases eingeführt und dort mit

der aus der Kathodengaszuführleitung (17) entnommenen Luft (16) verbrannt wird, um so ein Kathodengas zu erzeugen.

10. Vorrichtung nach Anspruch 9, **dadurch gekennzeichnet**, daß die sich von der Anodenkammer (3) zur Absorptionssäule (13a) erstreckende Anodenabgasleitung (9) mit einer Kondensator- und Trenneinrichtung (12) zum Isolieren des Dampfes aus dem Anodenabgas verbunden ist. 5
11. Vorrichtung nach Anspruch 9 oder 10, **dadurch gekennzeichnet**, daß das Anodenabgas oder Kathodenabgas dem Reformer (5) als Wärmequelle zum Aufrechterhalten der Reformierungstemperatur zugeführt wird. 10 15
12. Vorrichtung nach Anspruch 10 oder den Ansprüchen 10 und 11, **dadurch gekennzeichnet**, daß die Kondensator- und Trenneinrichtung (12) mit einer Dampfzuführleitung (21) verbunden ist, durch welche der Dampf, der aus einem Teil des kondensierten und separierten Wassers über einen Erhitzer (22) konvertiert wurde, zu einem oberen Strömungsteil der Anodengaszuführleitung (8) zurückgeführt wird. 20 25
13. Vorrichtung nach Anspruch 10 oder 12, **dadurch gekennzeichnet**, daß die Kondensator- und Trenneinrichtung (12) mit einer Dampfzuführleitung (21) verbunden ist, durch welche der Dampf, der durch einen Erhitzer (22) aus einem Teil des kondensierten und abgetrennten Wassers konvertiert wurde, zu der Zuführleitung (7) für das Brennstoffgas und den Dampf zurückgeführt wird. 30 35
14. Vorrichtung nach einem der Ansprüche 9 bis 13, **dadurch gekennzeichnet**, daß sie einen Stapel von Brennstoffzellen (30) mit interner Reformierung umfaßt und daß der Reformer (32) zwischen einem beliebigen Paar von Anodenkammer (3) und Kathodenkammer (4) angeordnet ist, um ein reformiertes Gas in die Anodenkammer (3) zu leiten. 40 45

Revendications

1. Une méthode de production d'énergie électrique à l'aide d'une pile à combustible de type carbonate en fusion (1) dans laquelle un gaz anodique est amené dans une chambre anodique (3) de ladite pile à combustible (1) et dans laquelle un gaz cathodique est amené dans une chambre cathodique (4), laquelle méthode comprend les différentes phases suivantes : 50 55

(A) introduction d'un gaz combustible et de vapeur dans une unité de reformage (5) en vue de reformer le gaz combustible avec de la vapeur pour obtenir un gaz anodique contenant du H_2 et du CO , et ensuite amené dudit gaz anodique dans la chambre anodique (3) de la pile à combustible (1) ;

(B) séparation du gaz carbonique du gaz anodique d'échappement de la chambre anodique; et

(C) recirculation du gaz d'échappement anodique duquel on a séparé l'oxyde de carbone au cours de la phase (B), dans la chambre anodique (3) par l'intermédiaire de l'unité de reformage comme gaz anodique; caractérisée par

(D) l'introduction de gaz carbonique dans de l'air après séparation du gaz d'échappement anodique et amené du gaz résultant de ce mélange dans un dispositif de combustion (27) tandis qu'une partie du gaz d'échappement anodique, duquel on a enlevé le gaz carbonique, est amenée à l'intérieur dudit dispositif de combustion (27) dans lequel ledit gaz subit une combustion, et le gaz de sortie du dispositif de combustion (27) est amené dans la chambre cathodique (4) comme gaz cathodique.

2. La méthode selon la revendication 1, caractérisée par le fait que la phase (B) est effectuée par contact vapeur/liquide entre le gaz d'échappement anodique et un liquide absorbant le gaz carbonique.

3. La méthode selon la revendication 2, caractérisée par le fait que le gaz d'échappement anodique est refroidi avant tout contact vapeur/liquide avec le liquide absorbant le gaz carbonique, la vapeur dans le gaz d'échappement anodique est condensée et séparée, et ensuite le contact vapeur/liquide entre le gaz d'échappement anodique et le liquide absorbant le gaz carbonique est effectué.

4. La méthode selon la revendication 2 ou 3, caractérisée par le fait que le liquide absorbant le gaz carbonique est une solution aqueuse d'un amine comme le diéthanolamine, une solution aqueuse de sel alcalin comme le carbonate de potassium, ou un mélange comprenant une solution aqueuse de sel alcalin et une solution aqueuse d'amine.

5. La méthode selon l'une des revendications 2 à 4, caractérisée par le fait que le liquide absorbant le gaz carbonique est isolé de la ligne d'écoulement du gaz d'échappement anodique

- après absorption du gaz carbonique pendant que de l'air est soufflé dans le liquide absorbant le gaz carbonique qui a absorbé le gaz carbonique pour dégager du gaz carbonique dudit liquide, et le gaz ainsi dégagé qui peut être un mélange de gaz carbonique et d'air peut être alimenté dans la chambre cathodique (4) comme gaz cathodique.
6. La méthode selon l'une des revendications 1 à 5, caractérisée par le fait que le gaz d'échappement anodique ou le gaz cathodique sont utilisés comme source de chaleur pour maintenir la température de reformage dans l'unité de reformage (5).
7. La méthode selon l'une des revendications 3 à 6, caractérisée par le fait qu'une partie de l'eau condensée au moment de la séparation est réchauffée jusqu'à son point de vaporisation puis est mélangée avec le gaz combustible.
8. La méthode selon la revendication 1, caractérisée par le fait que le gaz combustible, comme du méthane, est reformé avec de la vapeur dans une unité de reformage (5) de manière à obtenir un gaz anodique, et ledit gaz anodique est ensuite alimenté dans une anode de la pile à combustible, et le gaz d'échappement anodique duquel le gaz carbonique a été séparé au cours de la phase (B) est alimenté dans l'unité de reformage (5) avec le gaz combustible et la vapeur, et ensuite recirculé vers la chambre anodique (3).
9. Un appareil pour produire de l'énergie électrique comprenant :
- au moins une pile (1) à combustible au carbonate en fusion comprenant une plaque électrolyte imprégnée de carbonate en fusion (2) insérée entre une électrode anodique (3a) et une électrode cathodique (4a), chacune desdites deux électrodes (3a, 4a) étant dotée d'une chambre anodique (3) et d'une chambre cathodique (4) respectivement pour amener un gaz anodique et un gaz cathodique respectivement dans chacune desdites chambres; une ligne d'alimentation en gaz anodique (8) et une ligne de gaz d'échappement anodique (9) sont branchées respectivement à une entrée et à une sortie de la chambre anodique (3) de la pile à combustible (1) pour introduire à l'intérieur desdites chambres et évacuer à l'extérieur desdites chambres lesdits gaz respectivement;
 - une ligne d'alimentation en gaz cathodique (17) et une ligne de gaz d'échappement cathodique (24) branchées respectivement sur une

- entrée et une sortie de la chambre cathodique (4) de la pile à combustible (1) pour introduire dans ladite chambre et évacuer à l'extérieur de ladite chambre lesdits gaz respectivement;
- des moyens (7) d'alimentation de gaz combustible et de vapeur à l'intérieur de la ligne d'alimentation en gaz anodique (8) ; et
- un séparateur de gaz carbonique (13), caractérisé par le fait que ledit séparateur de gaz carbonique (13) comprend une colonne d'absorption (13a) dans laquelle le gaz d'échappement anodique de la ligne de gaz d'échappement anodique (9) est mis en contact avec un liquide absorbant le gaz carbonique par contact vapeur/liquide et ledit gaz produit par ladite absorption par contact est ensuite recirculé vers ladite unité de reformage (5), et
- un colonne de régénération (13b) branchée sur la ligne d'alimentation en gaz cathodique (17) dans laquelle le liquide chargé du gaz carbonique absorbé dans ladite colonne d'absorption (13a) est introduit, et ledit liquide est mélangé avec de l'air (16) alimenté par la ligne d'alimentation en gaz cathodique (17) de façon à faire dégager le gaz carbonique dudit liquide, tandis que ce liquide dont on a retiré et laissé se dégager le gaz carbonique est recirculé vers ladite colonne d'absorption (13a) ; et par le fait que ledit appareil comprend en outre un dispositif de combustion (27) branché sur la ligne d'alimentation en gaz cathodique (17) entre la colonne de régénération (13b) du séparateur de gaz carbonique (13) et la chambre cathodique (4) dans lequel dispositif de combustion (27) une partie du gaz d'échappement anodique s'acheminant de ladite colonne d'absorption (13a) vers l'unité de reformage (5) est introduite et soumise à une combustion avec de l'air (16) prélevé dans la ligne d'alimentation en gaz cathodique (17), de manière à produire un gaz cathodique.
10. L'appareil selon la revendication 9, caractérisé par le fait que la ligne de gaz d'échappement anodique (9), qui s'étend de la chambre anodique (3) à la colonne d'absorption (13a) est branchée à un moyen de condensation et de séparation (12) pour isoler la vapeur du gaz d'échappement anodique.
11. L'appareil selon la revendication 9 ou 10, caractérisé par le fait que le gaz d'échappement anodique ou le gaz d'échappement cathodique est introduit dans l'unité de reformage (5) comme source de chaleur pour maintenir la température de reformage.

12. L'appareil selon la revendication 10 ou selon les revendications 10 et 11, caractérisé par le fait que le moyen de condensation et de séparation (12) est branché à une ligne d'alimentation en vapeur (21) au travers de laquelle la vapeur obtenue par la conversion d'une partie de l'eau condensée et séparée par un réchauffeur (22) est recirculée vers une partie amont de la ligne d'alimentation en gaz anodique (8).
13. L'appareil selon la revendication 10 ou 12, caractérisé par le fait que le moyen de condensation et de séparation (12) est branché sur la ligne d'alimentation en vapeur (21) au travers de laquelle la vapeur obtenue par la conversion d'une partie de l'eau condensée et séparée par un réchauffeur (22) est recirculée vers la ligne d'alimentation en vapeur et en gaz combustible (7).
14. L'appareil selon l'une des revendications 9 à 13, caractérisé par le fait qu'il comporte un empilement de piles à combustible à reformage interne (30), et par le fait que l'unité de reformage (32) est placée entre une paire arbitraire de chambre anodique (3) et de chambre cathodique (4) pour l'amenée de gaz reformé dans la chambre anodique (3).

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A schematic diagram of a device 5. It is represented as a rectangular block with a cross-hatched interior region labeled 5a. Two input lines, labeled 7 and 9, enter the block from the left. A single output line, labeled 8, exits the block to the right.

FIG. 3

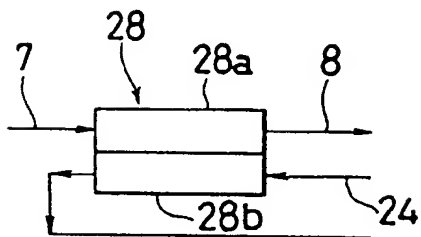


FIG. 4

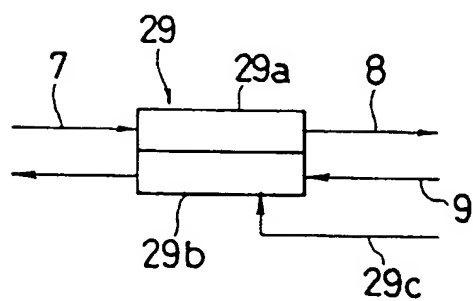


FIG. 5

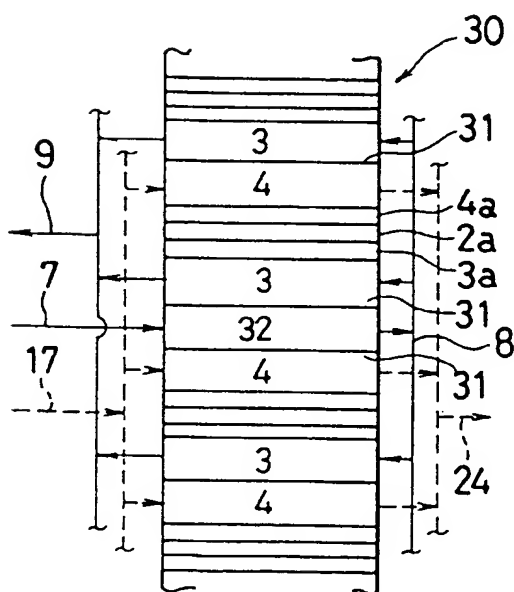


FIG. 6

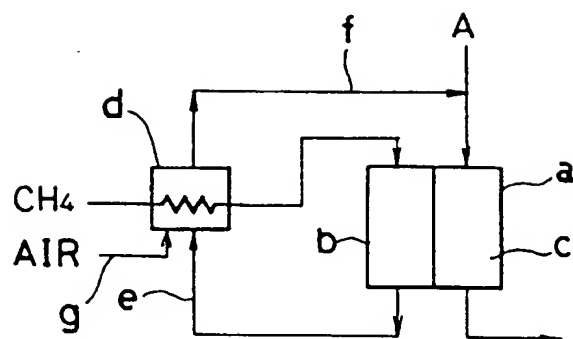
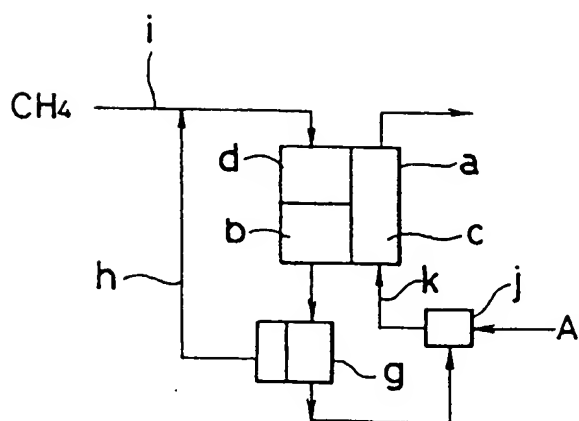


FIG. 7



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